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**SOLID-STATE  $^{15}\text{N}$  NMR OF  $^{15}\text{N}$ -LABELED NYLON 6 AND NYLON 11**

by

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# Solid State $^{15}\text{N}$ NMR of $^{15}\text{N}$ -labeled Nylon 6 and Nylon 11:

## Observation of Multiple Crystalline Forms and Amorphous Regions

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### ABSTRACT

The solid state  $^{15}\text{N}$  NMR characterization of nylon 6 and nylon 11 is reported. Nylon 6 (20%  $^{15}\text{N}$  enriched) was prepared by anionic polymerization of isotopically enriched caprolactam, and NMR samples were prepared by quenching from the melt, and by slow cooling and annealing. CP/MAS spectra of the  $^{15}\text{N}$  enriched samples showed a single sharp peak ( $\alpha$  crystal form) at 84.2 ppm (relative to glycine) and a broader resonance at 87.2 ppm. Relaxation experiments were conducted to determine  $T_{1\text{N}}$ ,  $T_{1\text{H}}$ , and  $T_{1\rho}$  for each sample at 300K. The crystalline resonance was found to have  $T_{1\text{N}}$ 's of 125-416s, while the downfield peak had two measurable  $T_{1\text{N}}$ 's, one component with  $T_1$  of 1-3s and a second with the longer  $T_1$  of 19-29s. The two components of the non-crystalline peak are thought to belong to a liquid-like amorphous region and a more rigid "interphase" region lying between the crystalline and amorphous regions.  $T_{1\rho}$  measurements were consistent with two-phase morphology although the two component decay for the amorphous region was not observed.  $^1\text{H}$   $T_1$  measurements were apparently dominated by spin diffusion that masked any differences between the regions.

The chemical shift anisotropy (CSA) of static samples were also obtained. Motion in the amorphous region was monitored by observing an isotropic peak at elevated temperatures. At temperatures above 100°C, the most deshielded ( $\sigma_{33}$ ) component was lost from the CSA spectrum suggesting a previously

unreported motion occurring in the rigid crystalline region. This motion is speculated to be associated with the intermolecular hydrogen bond between adjacent chains.

Polyundecanamide (nylon 11) was synthesized with 99+%  $^{15}\text{N}$  labeling of the amide nitrogen. Polymer samples were thermally treated to give the stable triclinic  $\alpha$ -crystal form. The  $\gamma$ -form was obtained by precipitation from neat trifluoroacetic acid upon evaporation.  $^{15}\text{N}$  CP/MAS NMR clearly differentiated the samples by chemical shift. The  $\alpha$ -crystal form transformed above  $95^\circ\text{C}$  to the pseudohexagonal  $\delta$ -crystal form, confirming previously reported x-ray and thermal analysis.  $^{15}\text{N}$  spin lattice ( $T_1$ ) relaxation experiments confirmed decreased relative mobility in going from the  $\delta$  to the  $\alpha$  form consistent with increased molecular rigidity and density. Previous studies suggested that the  $\alpha$ - $\delta$  transition involves the onset of rapid hydrogen bond disruption and reformation within the crystal lattice above the  $95^\circ\text{C}$  transition temperature.  $^{15}\text{N}$  chemical shift anisotropy (CSA) spectra showed that the hydrogen bonded amide units remain conformationally rigid in the crystal lattice despite increasing librational motion. Combining  $^{15}\text{N}$   $T_1$  information with wide-angle x-ray data, a model is presented which accounts for the crystal-crystal transition.



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## INTRODUCTION

High resolution solid state NMR is becoming an important tool for characterizing polymer systems. Cross polarization and magic angle spinning (CP/MAS) along with high power decoupling allow acquisition of high resolution spectra of natural abundance  $^{13}\text{C}$  nuclei with good sensitivity. The  $^{13}\text{C}$  solid state CP/MAS NMR of some important commercial polymers has improved our understanding of their microstructure and phase behavior [1-5]. Relaxation studies have identified non-crystalline regions poorly characterized by x-ray [3].

Recently, we have demonstrated that solid state CP/MAS NMR of natural abundance  $^{15}\text{N}$  is readily obtainable on solid polyamides [6,7]. In addition,  $^{15}\text{N}$  CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides; ie,  $\alpha$  and  $\gamma$  crystal forms. Resonances were observed for other regions which could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group potentially providing a tool for observing ordered region conformations in solid polyamides [8].

Although natural abundance spectra are attractive from a general utility point of view, the low sensitivity of nitrogen makes relaxation experiments ( $T_1$ ,  $T_{1\rho}$ ) time consuming or impossible on most instruments with most samples. Our interest in further examining the various crystalline and non-crystalline regions in polyamides by  $^{15}\text{N}$  CP/MAS prompted us to prepare isotopically enriched samples. We chose to prepare  $^{15}\text{N}$  enriched samples of nylon 6 and

nylon 11 because both are important commercial polyamides which have been thoroughly characterized in the solid state by many techniques (DSC, IR, x-ray) including solid state  $^{13}\text{C}$  NMR [4,5].

Laboratory preparation of each is relatively straight-forward and will be described in detail in future papers in this series. Isotopic enrichment for nylon 6 was accomplished starting with commercially available hydroxylamine hydrochloride (99%  $^{15}\text{N}$ ) and cyclohexanone [9]. The percent crystallinity was determined by DSC measurement of the heat of fusion for each sample as previously described [10]. Enriched nylon 11 was made using the readily available  $^{15}\text{N}$ -labeled phthalimide in a Gabriel synthesis starting from 11-bromoundecanoic acid and polymerization conditions previously described [11]. Here we report the  $^{15}\text{N}$  NMR characterization of various samples of the two nylons under a variety of conditions using several NMR methods.

## EXPERIMENTAL SECTION

### $^{15}\text{N}$ NMR Parameters

Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe. The  $^{15}\text{N}$  resonance frequency was 20.287 MHz and that of the  $^1\text{H}$  was 200.13 MHz. Samples were placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0 to 3.2 KHz with dry air. Crystalline glycine was placed in the rotor with the samples and used as an internal chemical shift reference (0 ppm). CP/MAS spectra were obtained with a standard crosspolarization pulse sequence using a

3.5  $\mu$ s  $^1\text{H}$  90° pulse and a mixing pulse of 2 ms. High power decoupling was used during a 50ms acquisition time with a nutating field of 62-68 KHz. Dipolar dephasing experiments were accomplished with the pulse sequence of Opella and Frey [12] with a delay ( $T_D$ ) of 20 to 100 $\mu$ s.

$^{15}\text{N}$  spin-lattice relaxation times ( $T_{1N}$ ) were obtained using the CP-90- $\tau$ -90 pulse sequence developed by Torchia [13]. Other relaxation measurements were obtained using appropriate pulse sequences for  $^1\text{H}$  180- $\tau$ -90 inversion recovery experiments (for measuring  $^1\text{H}$   $T_1$  by monitoring the  $^{15}\text{N}$  signal), and for obtaining  $^{15}\text{N}$  spectra without cross-polarization [3].

Peak deconvolution of the overlapping crystalline and amorphous resonances in the CP/MAS spectrum was accomplished using TENSOR, a Bruker-supplied Pascal program for simulating overlapping NMR resonances as combinations of Lorentzian or Gaussian lineshapes. The chemical shift anisotropy of static  $^{15}\text{N}$  spectra were simulated using POWDER, a Bruker Pascal program for simulating NMR lineshapes in solids. Both programs were run on an Aspect 3000 computer.

### Monomer and Polymer Syntheses

Potassium phthalimide (99.6%  $^{15}\text{N}$ ), 11-bromoundecanoic acid, anhydrous hydrazine, cyclohexanone and polyphosphoric acid were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin.  $^{15}\text{N}$  labeled hydroxylamine hydrochloride (99%  $^{15}\text{N}$ ) was obtained from ICON Services, Inc., Summit, New Jersey. Solvents and other materials were reagent grade and used as received. All

intermediates and products possessed physical properties consistent with expected structures and gave spectra identical to non-labeled materials. Details of the syntheses will be given in subsequent papers.

The crude polymer products were extracted overnight with methanol and dried under vacuum at 80 °C. NMR samples were prepared as follows: the polymer was placed between sheets of aluminum foil coated with a fluoropolymer mold release agent, then melt-pressed at 250 °C and 20,000 psi to give films of approximately 0.3mm thickness. The molten samples were either quenched in ice-cold water or annealed in the press at 160°C for 2 hours. The percent crystallinity was determined by DSC measurement of the heat of fusion for each sample as previously described.[10] A portion of the crude in situ nylon 6 reaction product was retained for comparison with methanol extracted samples.

## RESULTS AND DISCUSSION

### CP/MAS and $T_{1\rho}$ of Crystalline and Amorphous Nylon 6.

The CP/MAS spectrum of nylon 6 is shown in Figure 1. Only 18,000 scans were required to obtain excellent signal-to-noise for this 100mg sample. The spectrum shown is similar to natural abundance  $^{15}\text{N}$  spectra we previously reported [6,7]. The main strong peak clearly overlaps a broader resonance at lower field. The overlapping peaks were fit with a composite lineshape (Figure 2) and the individual components deconvoluted as shown. From the deconvoluted components, the upfield resonance is located at 84.2 ppm with a linewidth at half height of 2.4 ppm. This peak was previously correlated with



the  $\alpha$  crystal form of nylon 6 [6,7]. The broader downfield resonance is centered at 87.2 ppm and possesses a linewidth at half height of 6.3 ppm. This resonance had not been observed in our previous work with polyamides at the  $^{15}\text{N}$  natural abundance level. We believe this to be the signal from the non-crystalline or "amorphous" fraction of the nylon sample since its chemical shift appears midway between the  $\alpha$  and  $\gamma$  resonances typically observed for nylon 6 [6] and other nylons [7]. (The  $\gamma$  form gives a sharp resonance at 88.5 ppm [6]).

To conclusively identify the downfield resonance as that of the amorphous region, relaxation experiments were conducted to evaluate the mobility of each region by monitoring spin-lattice relaxation times ( $T_{1N}$ ). Using the method of Torchia [13], relaxation times  $T_{1N}$  were obtained at 300K for resonances at 84.2 ppm ( $\alpha$  crystal resonance) and 87.2 ppm (approximate position of the amorphous resonance) for several samples. Figure 3 displays the  $^{15}\text{N}$  spectra obtained with  $\tau$  delays shown. The downfield "amorphous" resonance decays rapidly while the crystalline peak at 84.2 ppm remains strong after 40 seconds. The crystalline component gave an excellent plot of magnetization decay for the annealed sample with a  $T_{1N}$  of 416s. The plot for the amorphous fraction of the same sample gave a two component decay with a  $T_{1N}$  values of 29.6s and 1.9s. The two shorter  $T_1$ 's for the 87.2 ppm is consistent with an amorphous fraction with much greater mobility than the crystalline portion of the sample. In addition, the detection of two  $T_{1N}$ 's may indicate two types of amorphous regions: a bulk amorphous fraction with liquid-like mobility and a non-crystalline "interphase" region with restricted motion. Similar phase morphology is observed in

polyethylene where the crystalline and the non-crystalline "interphase" region are clearly delineated by their  $T_{1C}$  relaxation times [3]. To our knowledge, this is the first report of NMR observation of an interphase region in a semicrystalline polyamide as well as the first relaxation measurements of crystalline and amorphous regions by  $^{15}\text{N}$  CP/MAS.

$^{15}\text{N}$   $T_1$  values are also reported in the Table 1 for the in situ prepared sample as well as methanol-extracted samples that were quenched from the melt. The amorphous regions in all samples have shorter relaxation times than the crystalline regions, a fact consistent with  $^{13}\text{C}$  relaxation studies of these materials [4]. In addition, the in situ prepared samples have shorter  $T_{1N}$  values than any of the methanol extracted samples. Since the  $T_{1N}$  values are associated with motions of the polymers, a shorter  $T_{1N}$  value for the in situ sample indicates more rapid motion, probably due to plasticization by residual caprolactam in the sample. Caprolactam has been shown to plasticize polyamides to improve flexibility and elongation [14,15]. Increased motion brought about by plasticization may account for the difference in relaxation times  $T_{1N}$  for the amorphous region. The increase in  $T_{1N}$  for the crystalline region of the unplasticized samples cannot be attributed to plasticizer effects. However, the process of extraction and heating of the sample may alter the size of crystalline domains. Spin lattice relaxation times of semicrystalline polymers have been shown to increase substantially with increasing crystal lamellar thickness [16]. The increase in  $T_{1N}$  on annealing the sample is consistent with increasing crystal lamellae thickness.

We took advantage of the difference in spin lattice relaxation times  $T_{1N}$  between the two phases to directly observe the amorphous fraction by obtaining the MAS spectrum of the  $^{15}\text{N}$  labeled nylon 6 without cross-polarization. By using a recycle delay of 5 to 10 seconds, the  $^{15}\text{N}$  magnetization in the crystalline regions is quickly saturated and the nuclei in the amorphous region with shorter  $T_{1N}$  can then be observed directly. Using this method, a spectrum of the amorphous region was obtained that was nearly identical to the deconvoluted peak from the CP/MAS spectrum shown in Figure 2; i. e. the resonance is broad and downfield of the  $\alpha$  crystal peak but upfield from the observed position of the  $\gamma$  crystal peak. Spectral subtraction gives a peak for the  $\alpha$  crystal form which is clearly seen as a symmetrical Lorentzian line (not shown) with contributions from the non-crystalline region removed.

### **Static Cross Polarization Spectra (Chemical Shift Anisotropy)**

The anisotropic chemical shifts (CSA) in solids can yield much information about the local electronic environment of a nucleus [17]. Although tensor elements have been estimated from the powder spectra of a number of  $^{15}\text{N}$  containing compounds [18,19], only one single-crystal  $^{15}\text{N}$  study has been reported for an amide (glycylglycine) giving tensor orientations with respect to bond angles [20]. This is not surprising since the random orientations of nuclei in semicrystalline polymers precludes absolute determination of tensor orientations with respect to the bond direction. Nevertheless,  $^{13}\text{C}$  CSA spectra of polymers can be sensitive to motions in the solid state [21].  $^{15}\text{N}$  CSA should

provide a superior method to  $^{13}\text{C}$  CSA for probing nylon 6 since only one chemically distinct nitrogen is present in the polyamide repeat unit. Recently the  $^{15}\text{N}$  CSA powder spectra of alanine-containing polypeptides were reported and both the tensor elements and isotropic chemical shifts found to be dependent on polymer conformation.[22]

A static  $^{15}\text{N}$  spectrum of nylon 6 which has been extracted with methanol is shown in Figure 4, lower trace. The upper trace in Figure 4 shows the calculated CSA powder spectrum at 300K. From POWDER calculations the individual tensors of the anisotropy were calculated:  $\sigma_{33}=5$  ppm;  $\sigma_{22}=60$ ppm;  $\sigma_{11}=180$ ppm. The calculated isotropic chemical shift ( $\sigma_{\text{iso}}$ ) is 81.6ppm, in good agreement with the value of 84.2 ppm obtained through MAS.

In an attempt to observe the amorphous fraction in the unplasticized static sample,  $^{15}\text{N}$  CSA spectra were obtained at various temperatures as shown in Figure 5. At 27°C, the non-axial powder pattern is seen. As the temperature is increased, a narrow amorphous resonance appears centered near 84 ppm. This peak becomes more intense at higher temperatures and is clearly seen above 100°C. The chemical shift of the amorphous fraction (84.3 ppm) approaches the isotropic chemical shift obtained through MAS. Rapid motion has averaged the anisotropy of the amorphous fraction.

Another interesting phenomenon is observed in the CSA spectra of Figure 5. As the temperature is increased from 27°C to 100°C, the downfield component of the powder pattern  $\sigma_{11}$  becomes smaller. At 115°C this component is either no longer sharply defined or has disappeared altogether. Note also

that the  $\sigma_{22}$  and  $\sigma_{33}$  elements remain essentially unchanged from the room temperature spectrum. This indicates a retention of non-axial symmetry since, in an axially symmetric pattern, the  $\sigma_{22}$  and  $\sigma_{11}$  elements should average to some intermediate value [17]. Although the pattern remains non-axially symmetric, the loss of the  $\sigma_{11}$  component at elevated temperature suggests the onset of motion associated with some tensor component of the amide nitrogen.

Interestingly, the tensor element  $\sigma_{11}$  associated with this component has been shown to lie nearly parallel to the NH bond in amides [20]. This suggests a change in intermolecular hydrogen bonding at elevated temperatures. An infrared study of the effect of temperature on hydrogen bonding in amorphous nylons by Skrovanek and coworkers [23] found that the amide groups remain nearly 100% hydrogen bonded at temperatures up to 210 °C. The average hydrogen bond strength, however, was shown to decrease. Frequency shifts and changes in absorbtivity in the IR were attributed to relatively large vibrational displacements of the NH bond [23]. In the crystalline region of the polyamide, the relatively small hydrogen will have the best chance for rapid motion even in the solid lattice. The concept of a "mobile" hydrogen that oscillates at a frequency sufficient to attenuate the  $\sigma_{33}$  component alone is consistent with the remaining crystalline components of the CSA spectrum at 150 °C.

This argument is further supported by dipolar dephasing experiments on the in situ prepared nylon 6 samples at 300K (Figure 6) and 350K (Figure 7). The upper trace in each experiment shows the normal CP/MAS result. The lower trace shows the dephasing due to dipolar coupling with a  $T_D$  of 100  $\mu$ s.

After removing the caprolactam by extraction, only a small fraction of the signal remains. This indicates that strong dipolar coupling between  $^{15}\text{N}$  and the attached  $^1\text{H}$  returns to attenuate the signal.

At 370K (upper limit for MAS with our probe) the dipolar dephasing experiment (Figure 8) shows a small resonance remaining at  $T_D$  of 120  $\mu\text{s}$ . At this temperature, enough motion is present to weaken the dipolar interaction such that the signal is not completely lost. Note that the chemical shift does not change significantly throughout the experiment. The peak which remains may be argued to be part of the amorphous phase which now has more liquid-like mobility. Our relaxation experiments, however, confirm the remaining peak to be correlated with the  $\alpha$  crystal form and not the amorphous region. The fact that significant motion can occur in the crystalline region to diminish the dipolar interaction tends to support the "mobile" proton model.

### $T_{1H}$ and Spin Diffusion

$T_{1H}$  measurements were made at temperatures of 300K and 350K. The  $T_{1H}$  values were obtained by measuring the recovery of the  $^{15}\text{N}$  magnetization at different  $\tau$ . Since the  $^{15}\text{N}$  resonances were already determined for the crystalline and amorphous components, the proton relaxation of each phase can be measured indirectly by observing the decay in  $^{15}\text{N}$  magnetization. The  $T_{1H}$  values of the in situ sample and the extracted sample are shown in Table 1.

The  $^1\text{H}$   $T_1$  values for each sample are about 1 second, very close to those for the crystalline region of polyethylene [3]. Unlike polyethylene, which

contains a very liquid-like amorphous region with a much shorter  $T_{1H}$ , the amorphous region of nylon 6 has very nearly the same  $T_{1H}$ . The fact that the two phases have very different  $T_{1N}$  but similar  $T_{1H}$  indicates rapid  $^1H$  spin diffusion between the phases. To confirm that the fast  $^1H$  spin diffusion observed was not unique to the  $^{15}N$  nucleus, the analogous relaxation experiment observing the  $^{13}C$  nucleus was performed.  $^{13}C$  resonances for the crystalline and amorphous regions (previously identified by Veeman [4]) were measured. Nearly identical  $T_{1H}$  values were obtained confirming the presence of rapid spin diffusion between phases.

### $T_{1\rho}$ Measurements

$T_{1\rho}$  measurements were made using pulse sequence II and are also reported in Table 1. The crystalline region has the longer relaxation time (13-58 ms) and the amorphous region the shorter (0-40 ms). Although the increase in relaxation times  $T_{1\rho}$  correlates with increasing percent crystallinity, the large differences in relaxation times seen for  $^{15}N$   $T_1$  are not evident. The reason for this has been discussed by several authors studying semicrystalline polymers by  $^{13}C$  CP/MAS [24-26]. They point out that rotating frame relaxation ( $T_{1\rho}$ ) is not pure spin-lattice in nature but has a considerable spin-spin component due to rapid  $^1H$  spin diffusion between the different phases [25]. In highly crystalline systems, the rotating frame relaxation was found to be completely dominated by spin-spin relaxation [26]. In such systems, the  $T_{1\rho}$  of the crystalline phase is usually shorter than the amorphous region because of more efficient  $T_2$  in the

crystalline region. In these nylon 6 samples, spin diffusion, although highly evident in the nearly identical  $T_{1H}$  values for both the crystalline and amorphous phases, does not dominate  $T_{1\rho}$ . Nevertheless, the two amorphous components seen in the  $T_{1N}$  relaxation experiment are not evident from  $T_{1\rho}$  measurements.

Although information gained from the  $T_{1\rho}$  experiment is somewhat limited by  $^1H$  spin diffusion (in this case), the relative values for  $T_{1\rho}$  may contain information about plasticization of the amorphous phase.  $^{13}C$   $T_{1\rho}$  measurements of other polymers confirm that plasticizers act to increase molecular mobility and reduce the relaxation time [27]. Since the plasticizer occupies only the amorphous region, it should be possible to monitor the motion of the amorphous region by observing the  $T_{1\rho}$  of the downfield non-crystalline resonance. Values reported in Table 1 for  $T_{1\rho}$  of the amorphous as well as the crystalline regions show shorter values for the plasticized in situ prepared sample than for the extracted sample. The amorphous peak for the plasticized sample decayed so rapidly into the noise level of the spectrum that accurate determination of  $T_{1\rho}$  for this peak was not possible. Once the plasticizer is removed, the  $T_{1\rho}$  increases substantially. Similar to the  $T_{1N}$  data, the increase in  $T_{1\rho}$  of the crystalline component may be related less to plasticizer effects and more to changing crystallite size.



## Nylon 11 Results

### CP/MAS Spectra

The  $^{15}\text{N}$  CP/MAS spectrum of nylon 11 annealed at  $170^\circ\text{C}$  is shown in Figure 9, trace A. The most intense resonance is seen at 84.2 ppm (downfield of glycine at 0 ppm) with a broad shoulder further downfield. The main resonance was identical to that previously found for the  $\alpha$  crystal form of nylon 6 [6] and a variety of other nylon samples [6,7]. The downfield resonances have not been previously assigned to any particular crystal form although the "amorphous" region of nylon 6 was observed as a broad resonance centered in this region. Using a  $90^\circ$   $^{15}\text{N}$  pulse with decoupling, the MAS spectrum in trace B was obtained. The  $\alpha$  crystal magnetization has been saturated, leaving only the fast relaxing "amorphous" component shown in trace B. Spectral subtraction of B from A gives the narrow  $\alpha$  crystal resonance seen in trace C at 84.2 ppm. Trace D shows the CP/MAS spectrum of the annealed sample obtained at 388K ( $115^\circ\text{C}$ ), well above the reported  $\alpha$  to  $\delta$  transition temperature. Clearly the peak for the  $\alpha$  crystal form has disappeared, leaving only downfield resonances at 85.5 and 86.7 ppm. On cooling, the spectrum becomes identical to trace A again, confirming the reversibility of the  $\alpha$ - $\delta$  transition.

The  $^{15}\text{N}$  CP/MAS spectrum of nylon 11 quenched from the melt ( $\delta'$  crystal form) shows a single sharp peak at 86.6 ppm and the  $\alpha$  crystal form resonance is absent, confirming x-ray and thermal analysis results on quenched samples. This peak appears at the same chemical shift as the  $\delta$ -form in the annealed sample (Figure 9). The kinetic stability of the  $\delta'$  crystal form is confirmed by

heating to 107°C; the peak appears to narrow but the chemical shift remains identical. Extended annealing at elevated temperatures is required to convert the  $\delta'$  form to the more stable  $\alpha$  form. Although the relative thermodynamic stability of  $\delta$  and  $\delta'$  forms are quite different, even at 107°C, the average conformations of the amide groups in each are apparently similar at the molecular level as evidenced by  $^{15}\text{N}$  NMR.

In the spectra of both quenched and annealed nylon 11, a broad peak centered at 86.5-87 ppm is seen for the amorphous fraction of the polyamide overlapping the peaks of the  $\delta$  and  $\delta'$  crystal forms. It was initially unclear how the  $\delta$  and  $\delta'$  morphologies were different from the bulk amorphous material. Spin lattice relaxation  $T_{1N}$  experiments were performed on both annealed and quenched samples to evaluate the relative mobilities of each phase. The results are shown in Table 2. As expected, the  $\alpha$ -crystal form possesses the longest  $T_{1N}$ , consistent with its highly ordered structure. The relaxation data for the  $\delta$ - and  $\delta'$ -forms (86.6 ppm) were found to both fit a bi-exponential relaxation curve indicative of at least two components with different relaxation times. The short component times (2-7s) are similar to that obtained for the bulk amorphous fraction of nylon 6. The long  $T_1$  component of this resonance varies greatly between samples, and may depend on crystallite size. For the  $\delta$ -form, the relaxation time  $T_{1N}$  is 112s while that of the  $\delta'$ -form is 13s. The longer  $T_{1N}$  for the  $\delta$ -form indicates that, while the amides in the  $\delta$  and  $\delta'$ -crystals may be similar chemically, the relative mobility of the  $\delta'$ -form is much greater than that of the  $\delta$ -form. The  $\gamma$  crystal form value is given for

comparison. The long  $T_{1N}$  confirms that this is a crystalline resonance although, like the other semicrystalline samples, it contains a broad shoulder centered about 86.6 ppm characteristic of the amorphous fraction. The chemical shift of the crystalline peak (88.8 ppm), however, is clearly different from any of the other crystal forms discussed so far. The combination of  $^{15}\text{N}$  chemical shift coupled with  $T_{1N}$  measurements allows clear and concise identification of all four individual crystal forms and the amorphous regions of various nylon 11 samples making this one of the most versatile methods for solid state characterization of polyamides.

The subject of rapidly re-orienting hydrogen-bonds in the  $\delta$ -form has been discussed in a model requiring rapid molecular motion without destroying the crystal structure [28]. Such a model has been used to explain the Brill transition seen in nylon 66 [29]. English and coworkers have recently studied segmental motion in nylon 66 using deuterium NMR [30]. While the methylene groups between amide units were found to have substantial librational motion well below the melting point, no evidence for amide reorientation was observed. In fact, the amide N-D bond in nylon 66 was shown to remain in a rigid lattice up to just below the melting point, although some librational motion was observed. This result casts doubt on such motion occurring above the  $\alpha$ - $\delta$  transition in nylon 11.

To further examine the possibility of rapid hydrogen-bond reorientation in nylon 11, static chemical shift anisotropy (CSA) spectra were obtained at various temperatures on the  $\alpha$ -form nylon 11 sample obtained by annealing at 170°C.

Increased molecular motion has been shown to cause narrowing of the  $^{13}\text{C}$  CSA spectra of various semicrystalline polymers [20]. The  $^{15}\text{N}$  CSA spectra of annealed nylon 11 obtained at several temperatures are similar in shape and chemical shift range to those observed for low molecular weight model amides [17-19] and those obtained for nylon 6. At temperatures above the  $T_g$ , the amorphous component spectrum collapses to a relatively narrow resonance in the center of the still rigid crystalline CSA pattern. The relative intensity of the crystalline and amorphous components varies with temperature, precluding quantitation [31]. Most important for this sample, however, is that the crystalline component shows no evidence of narrowing at the  $95^\circ\text{C}$   $\alpha$ - $\delta$  transition. Even heating up to 420K ( $147^\circ\text{C}$ ) failed to narrow the crystalline CSA pattern. The  $^{15}\text{N}$  CSA data, coupled with the deuterium NMR results for nylon 66, argues against rapid reorientation of hydrogen bonds in the crystal. Intuitively, motion of the amide groups in the crystalline regions should occur only after melting since the loss of this high-energy intermolecular interaction should allow molecular motion.

As mentioned, deuterium NMR studies of nylon 66 have shown that large amplitude librations of the methylene chains can occur well below the polymer melting point [30]. Such motions may be responsible for the transition seen in nylon 11; i.e., rapid wagging motion of methylene groups could result in a change in the crystal structure or dimensions without completely disrupting the long range order maintained by the hydrogen bond lattice. Rapid librations would also be consistent with decreases in spin lattice relaxation times for the

observed crystal resonances. Such a model is supported by x-ray data given in Table 3. Interchain distance in the  $d_{010}$  direction increases between the  $\alpha$  and  $\delta$ -forms. At the same time, the  $d_{001}$  distance along the chain axis decreases from 12.1Å to 11.3Å. A proposed model to account for the crystal-crystal transition without disruption of the in-plane hydrogen bonding involves rapid methylene segment librations that expand the crystal structure from the triclinic  $\alpha$ -form to the pseudohexagonal  $\delta$ -form. It should be noted that motions of this type are not trans-gauche transitions, but are large amplitude librations of the chain within the crystal lattice [30]. Note also that the layer-like hydrogen bonded structure can be maintained in both forms although the interchain distance increases somewhat. This is consistent with the rapid reformation of the  $\alpha$ -form on cooling back below the 96°C transition temperature. The stability of the hydrogen bonded sheets is further supported by the failure of the CSA to narrow at temperatures even up to just below the polymer melting temperature. Moreover, this model is intuitively reasonable since such strong intermolecular interactions should be disrupted only at the melting point.

## CONCLUSIONS

The  $^{15}\text{N}$  labeled nylon 6 sample was prepared in good yield by anionic polymerization of the labeled caprolactam monomer. Enrichment of approximately 20%  $^{15}\text{N}$  has allowed direct  $T_{1\rho}$  and  $T_{1\rho}$  relaxation measurements as well as  $T_{1H}$  determination by indirect observation of  $^{15}\text{N}$  cross polarization. The rigid crystalline region has a much longer  $T_{1\rho}$  relaxation than the more

mobile amorphous region with a  $T_{1N}$  of 111-416s. Two components were observed in the relaxation of the amorphous peak: a rapidly relaxing component with  $T_1$  of 1-3s and a slower component with  $T_1$  of 19-29s. The two non-crystalline components are thought to belong to amorphous and non-crystalline "interphase" regions, respectively.

Less dramatic behavior is seen in  $T_{1\rho}$  relaxation times. Only a single amorphous component could be observed. This anomaly is attributed to considerable  $^1\text{H}$  spin-spin relaxation within the sample resulting in similar  $T_{1\rho}$  values. This conclusion is further supported by  $^1\text{H}$   $T_1$  relaxation experiments which show that rapid  $^1\text{H}$  spin diffusion is occurring between the phases.

The first chemical shift anisotropy patterns of nylon 6 and nylon 11 are reported. The CSA powder patterns of nylon 6 show the growth of an amorphous signal at elevated temperatures with a chemical shift near the isotropic value obtained with MAS. The  $\sigma_{11}$  component becomes less prominent with increasing temperature and finally disappears above 115°C. The identity of this component has not been previously reported, but is speculated to be associated with the tensor component along the NH bond of the amide group. At elevated temperatures, motion involving vibration or libration of the hydrogen atoms in the still rigid hydrogen-bonded crystalline portion of the sample causes disappearance of this tensor component.

Polyundecanamide (nylon 11) was readily synthesized with 99+%  $^{15}\text{N}$  labeling of the amide nitrogen. Polymer samples were thermally treated to give the stable triclinic  $\alpha$ -crystal form and precipitated from trifluoroacetic acid to

give the  $\gamma$ -form.  $^{15}\text{N}$  CP/MAS NMR coupled with spin lattice relaxation ( $T_{1\rho}$ ) measurements clearly differentiated the polymer morphologies. The  $\alpha$ - and  $\gamma$ -forms displayed values similar to those observed for nylon 6 and many other nylons. The  $\alpha$ -crystal form transforms above 95°C to the pseudohexagonal  $\delta$ -crystal form, confirming previously reported x-ray and thermal analysis results for nylon 11.  $^{15}\text{N}$  spin lattice relaxation experiments were used to observe the relative mobility of the phases, with the relative molecular order and  $T_{1\rho}$  values increasing in going from the  $\delta$  to the  $\alpha$  form. Unlike previous studies in which hydrogen bonds were postulated to break and reform rapidly above the 95°C transition,  $^{15}\text{N}$  chemical shift anisotropy (CSA) spectra show that the hydrogen bonded amide units are rigidly oriented in the crystal lattice. Combining  $^{15}\text{N}$   $T_1$  information with wide-angle x-ray data, a model is presented involving methylene chain and amide libration which accounts for the crystal-crystal transition as well as the relative stability of the various crystal forms.

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**TABLE 1. Relaxation times for Nylon 6 samples.**

<u>Sample</u>	<u>% xtal</u>	<u>Parameter</u>	<u>Amorphous (87.2ppm)</u>		<u>Crystalline (84.2ppm)</u>
In situ	23	$T_{1N}$	----- <sup>a</sup>	26s	111.5s
		$T_{1H}$		0.99s	0.95s
		$T_{1p}$		----- <sup>b</sup>	13.8ms
Quenched	29	$T_{1N}$	2.7s	19s	230s
		$T_{1H}$		1.06s	1.03s
		$T_{1p}$		24.3ms	44.5ms
Annealed (160°C)	45	$T_{1N}$	1.9s	29.1s	416s
		$T_{1H}$		0.75s	0.78s
		$T_{1p}$		37.9ms	57.7ms

<sup>a</sup>Short  $T_1$  component was not observed for this sample.

<sup>b</sup>Decayed too rapidly to be observed.



**Table 2.  $^{15}\text{N}$  Spin Lattice Relaxation Times ( $T_{1\text{N}}$ ) and Chemical Shifts<sup>a</sup> for Nylon 11**

<u>Sample</u>	<u>Form</u>	<u>88.8 ppm</u>	<u>86.6 ppm<sup>b</sup></u>	<u>84.2 ppm</u>
Annealed	$\alpha$	-----	4.9s; 68.1s	178.3s
Annealed (373K <sup>c</sup> )	$\delta$	-----	7.2s; 112.2s	
Quenched in Dry Ice/i-PrOH	$\delta'$	-----	2.3s;13.4s	-----
$\text{CF}_3\text{CO}_2\text{H}$ ppt	$\gamma$	84.1s	4.2s; 19.5s	-----

<sup>a</sup>Downfield of solid glycine

<sup>b</sup>This region also contains resonances for "amorphous" nylon

<sup>c</sup> $T_{1\text{N}}$  acquisition temperature

**Table 3. Crystalline System and Unit Cell Dimensions for Nylon 11**

Crystal Form	Crystal System	(Chain Axis)	(Chain Packing)		Ref.
		$d_{001}$	$d_{010}$	$d_{100}$	
$\alpha$ crystal form	triclinic	12.1Å	3.62Å	4.40Å	1-4
$\delta$ crystal form	pseudohexagonal	11.3Å	4.16Å	4.16Å	6,8
$\delta'$ smectic form	pseudohexagonal	11.3Å	4.11Å	4.11Å	8

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## LIST OF FIGURES

- Figure 1.**  $^{15}\text{N}$  CP/MAS spectrum (18,000 FID's) of  $^{15}\text{N}$  enriched nylon 6 showing  $\alpha$  crystal form (large peak at approximately 84 ppm) and broader, overlapping region downfield (non-crystalline region).
- Figure 2.** TENSOR fit of the  $^{15}\text{N}$  CP/MAS lineshape of nylon 6. The bottom traces show the calculated fit along with the individual components.
- Figure 3.**  $^{15}\text{N}$  spectra obtained from the CP  $T_1$  pulse sequence of Torchia with  $\tau$  delays shown. The lower trace ( $\tau = 40\text{s}$ ) shows mainly the crystalline component with long  $T_{1\text{N}}$ .
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- Figure 6.**  $^{15}\text{N}$  dipolar dephasing spectrum of in situ prepared nylon 6 at 300K. Upper trace:  $T_{\text{D}} = 20$  microseconds with magnetization intact. Lower trace:  $T_{\text{D}} = 100$  microseconds with rigid components dephased.

- Figure 7.**  $^{15}\text{N}$  dipolar dephasing of in situ prepared nylon 6 at 350K. Upper trace:  $T_D = 20$  microseconds. Lower trace:  $T_D = 100$  microseconds showing mobile regions due to molten caprolactam.
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- Figure 9.**  $^{15}\text{N}$  NMR spectra of isothermally annealed nylon 11. Trace A is the CP/MAS spectrum obtained at 300K. Trace B was obtained by applying a  $90^\circ$   $^{15}\text{N}$  pulse with proton decoupling to saturate the crystal resonance. Trace C is the difference spectrum of A and B showing only the  $\alpha$  crystal resonance at 84.2 ppm. The  $\alpha$  crystal resonance disappears on heating above the  $95^\circ\text{C}$  (368K)  $\alpha$ - $\delta$  transition temperature to give the  $\delta$  form seen in trace D.

Figure 1

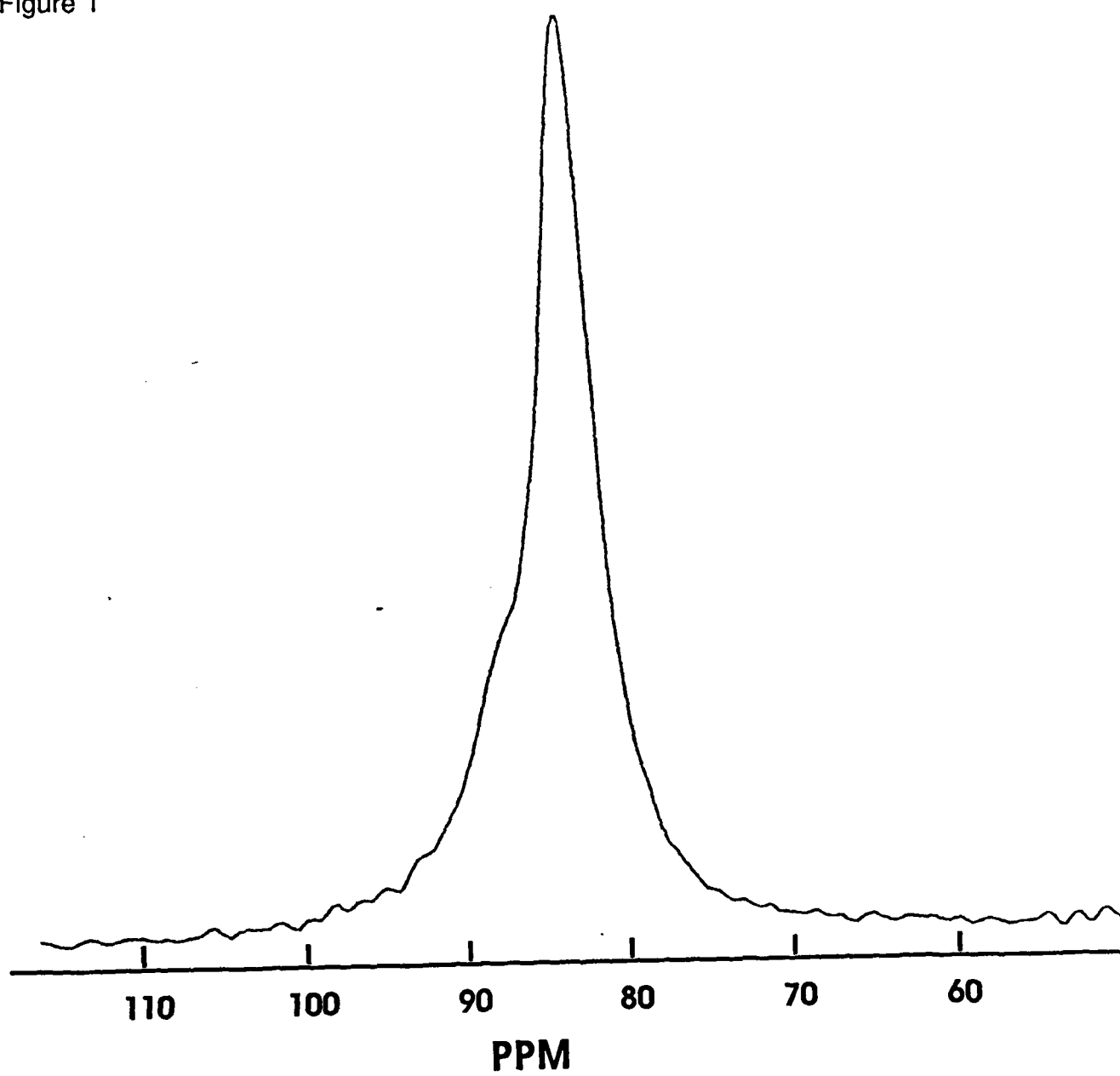




Figure 2

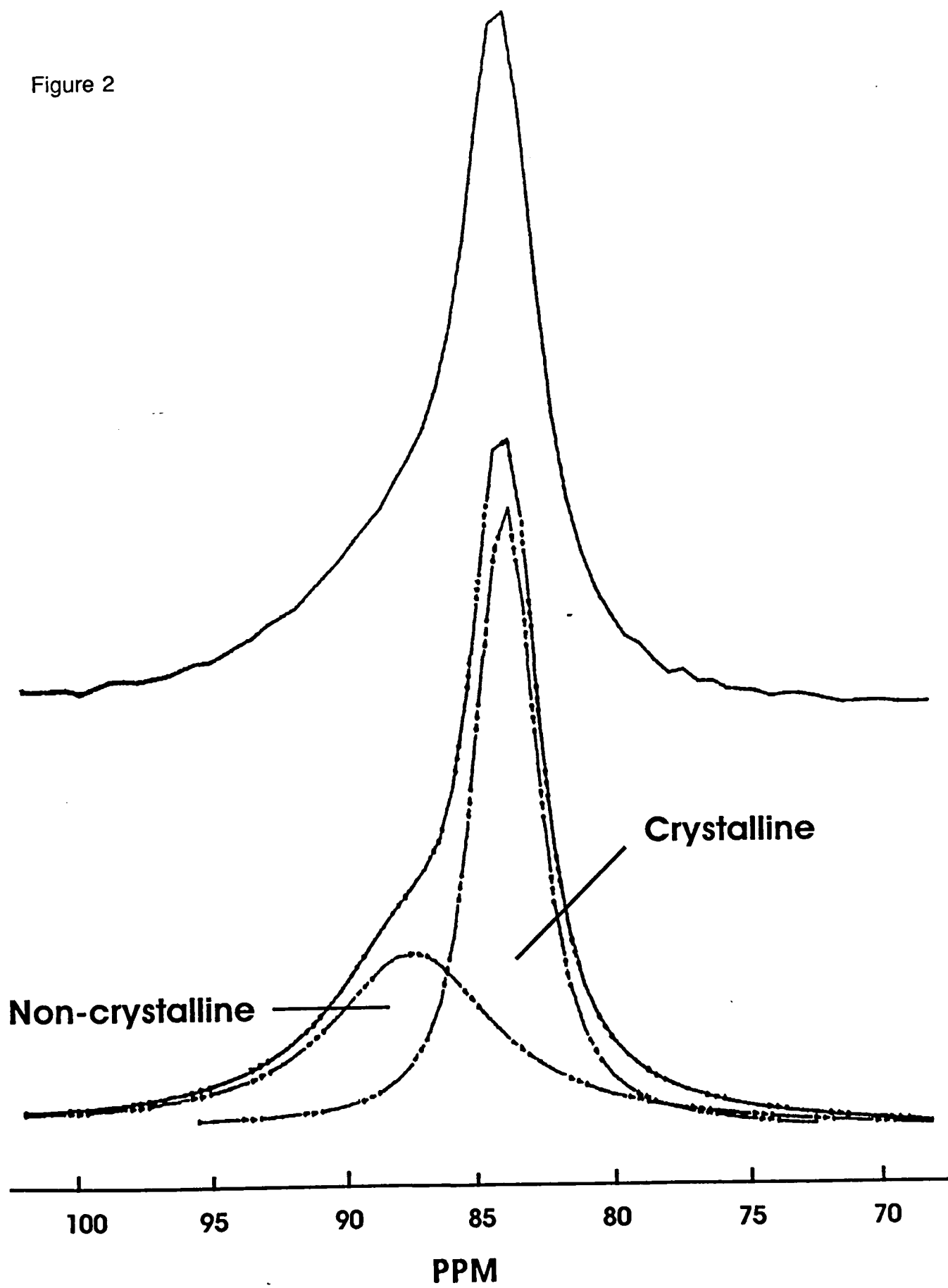


Figure 3

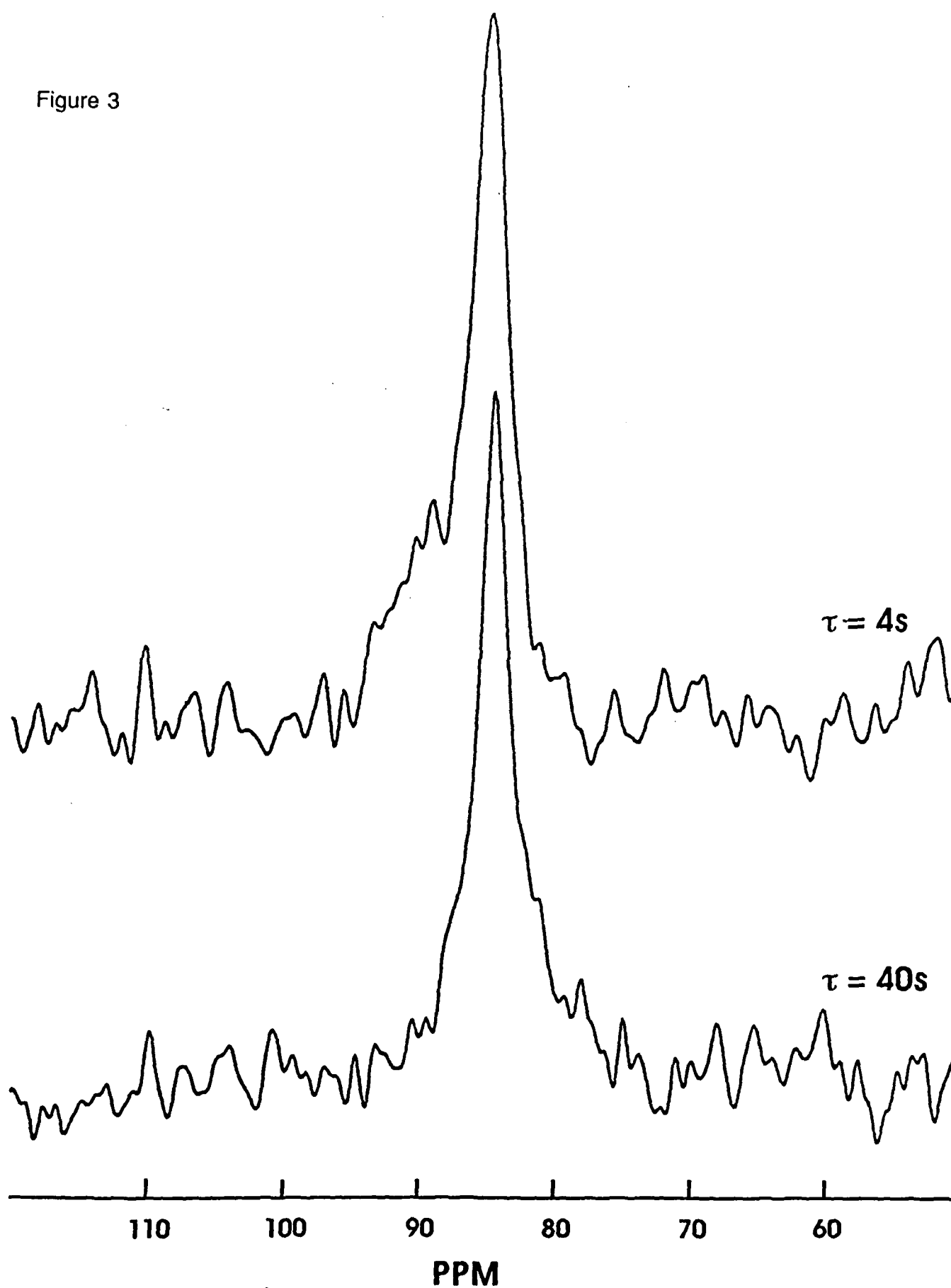


Figure 4

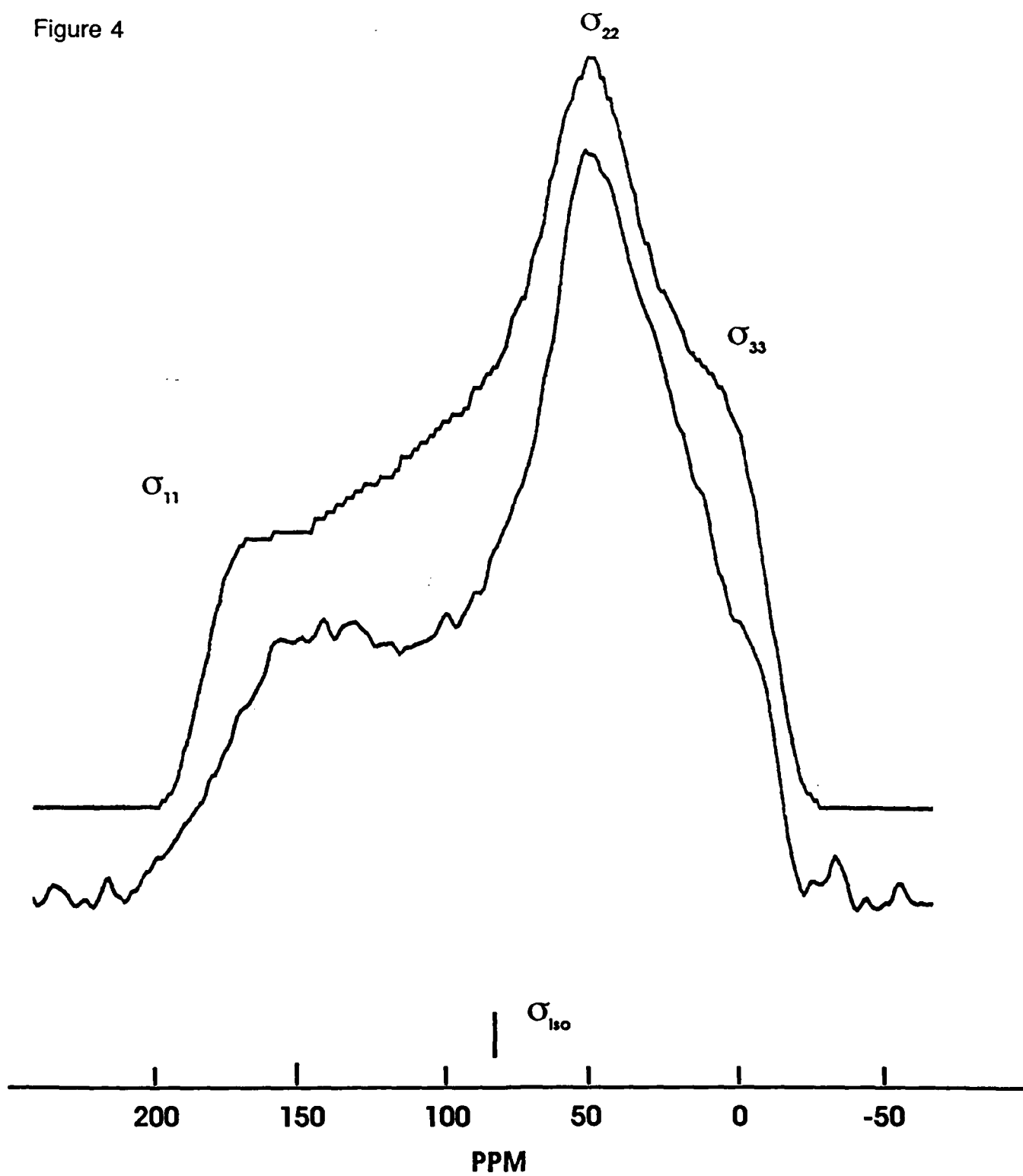


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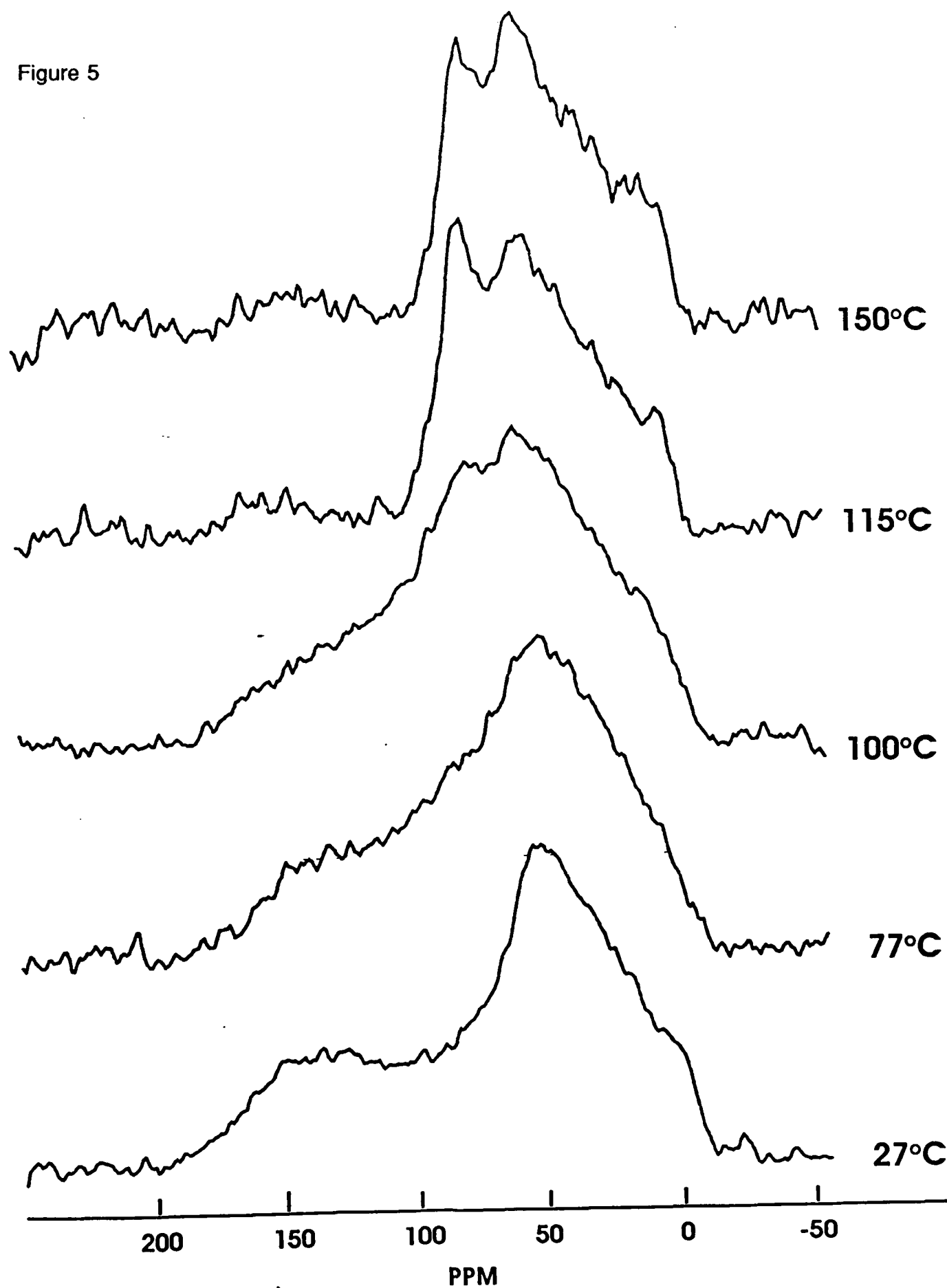


Figure 6

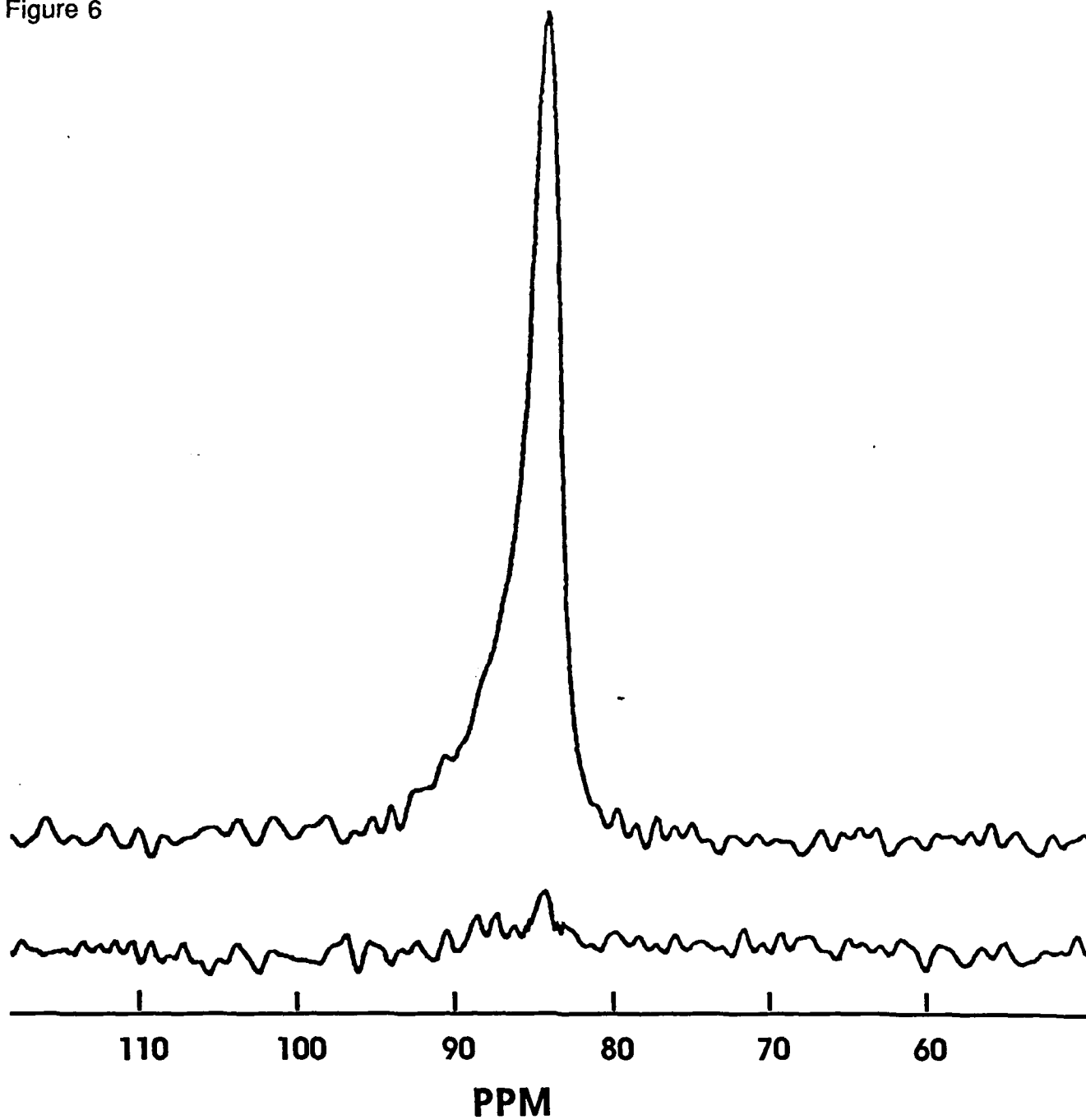


Figure 7

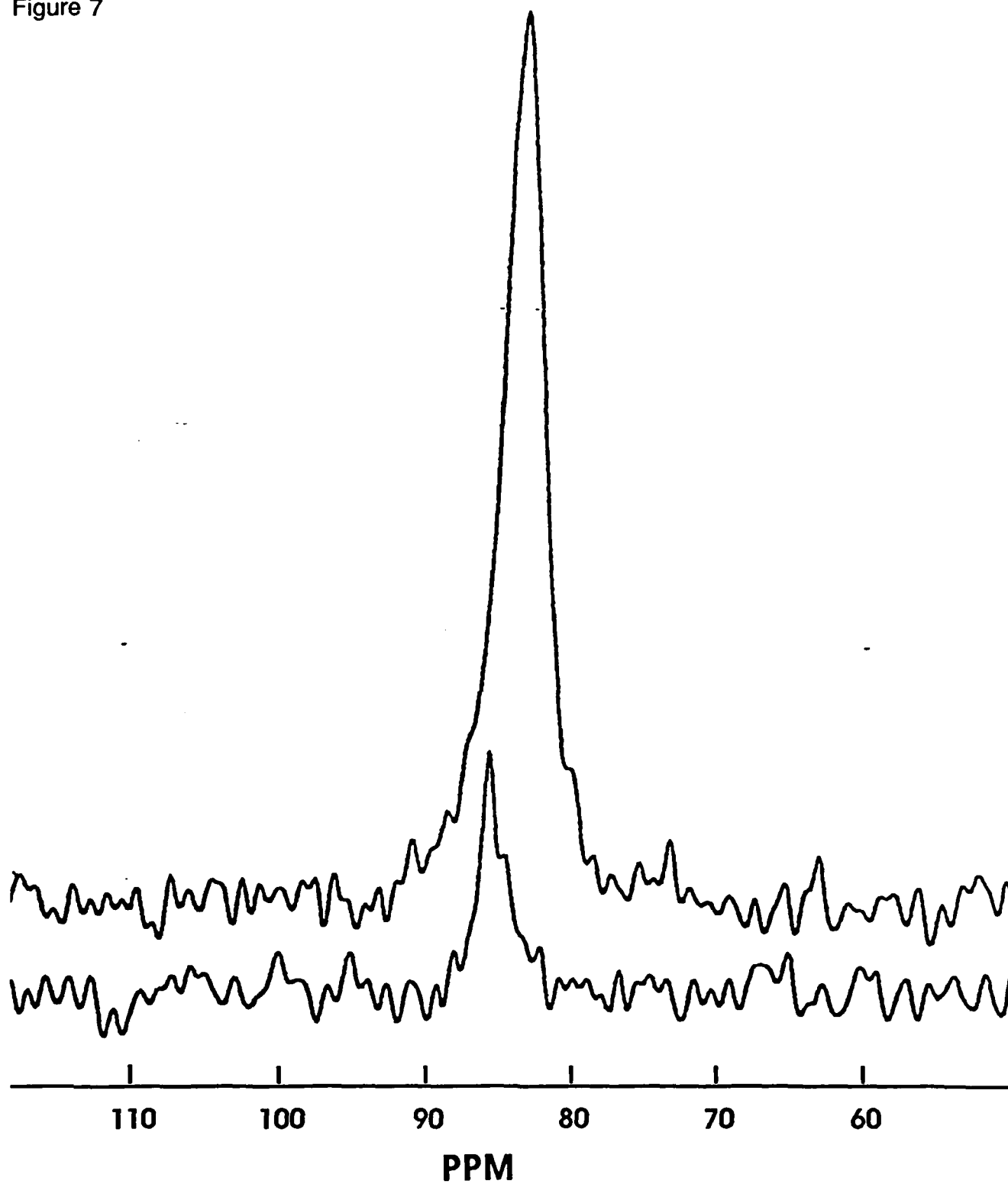


Figure 8

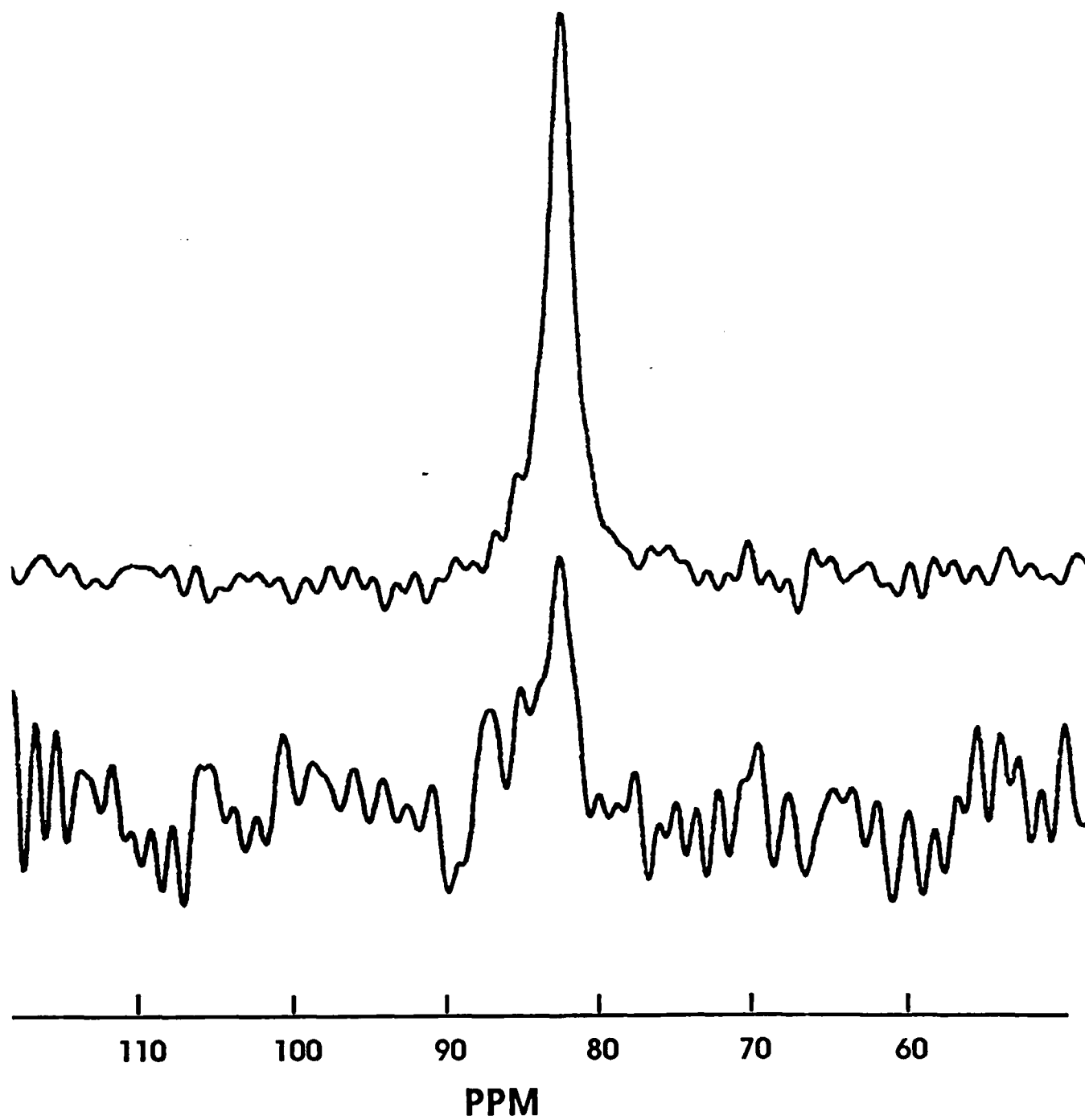


Figure 9

